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INFLUENCE OF ANION NUCLEOPHILICITY ON THIOUREA DECOMPOSITION AT THE BATH CHEMICAL DEPOSITION OF PbS AND $Cd_xPb_{1-x}S$ FILMS

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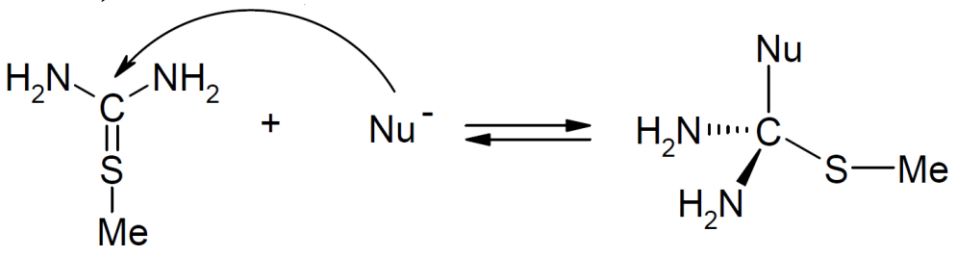
Abstract. The influence of anion component of metal salts on chemical and phase composition, structure and properties at bath chemical deposition of PbS films and $Cd_xPb_{1-x}S$ solid solutions by thiourea is almost not discussed in literature. However, the impact of anion on film crystallization is known rather well, and the nature of impurity including the anion nature, influences noticeably on structure and morphology of microcrystals. To understand the role and the mechanism of anion action series of experiments on chemical deposition of PbS in the presence of sodium salts (NaCl, NaBr, NaI, Na_2SO_4, $NaCH_3COO$, $NaNO_3$) and $Cd_xPb_{1-x}S$ solid solutions with different cadmium salts were carried out.

Hydroxyl ion plays an essential activation role at thiourea decomposition. The mechanism of decomposition of thiourea from the positions of nucleophilic addition of hydroxyl ion on thiocarbonyl atom of carbon can be expanded due to addition to thiourea other nucleophiles Nu (SO_4^{2-},NO_3^-, CH_3COO^-, Cl^-, Br^-, I^-):



The increase of anion nucleophilicity at transition from I^- to SO_4^{2-}-ion leads to the increase of reactivity of activated thiourea due to weakening of carbon – sulfur bond. It is experimentally confirmed by first-order reaction rate constants of thiourea decomposition in the reaction of PbS formation in the presence of sodium salts which are ranked as $k_{I^-} > k_{Br^-} > k_{Cl^-} > k_{NO_3^-} > k_{CH_3COO^-} > k_{SO_4^{2-}}$.

This series is practically in accordance with the established enrichment level of $Cd_xPb_{1-x}S$ solid solution with cadmium sulfide when using various cadmium salts in the reaction mixture: $CdSO_4$> $Cd(NO_3)_2$> $Cd(CH_3COO)_2$ > $CdCl_2$ > $CdBr_2$ >CdI_2.

Therefore it is possible to note that the structure of the reaction complex Me – N_2H_4CS – An has an immediate influence on the formation of both PbS films and $Cd_xPb_{1-x}S$ solid solutions. The joint analysis of the experimental results and the mechanism of film formation on the basis of nucleophilic addition of anion to thiourea allows to consider that the nucleophilicity of the studied anions from iodide- to sulfate-ion leads to the increase of reactivity of activated thiourea due to weakening of carbon – sulfur bond.

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